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Colloid Transport in Saturated Fractured Media: Experimental and Numerical Investigations using Synthetic and Natural Fracture Materials

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Outline

- Research Goals
- Experimental methods
- Interpreting experiment results: challenges and potential numerical solution
- Differentiating tailing due to dispersion from tailing due to filtration – coupled numerical and experimental approach
  - Numerical methods
  - Experimental methods
  - Results
- Summary and Future Work

Research Goals

- Establish a mechanistic relationship between flow rate (Q), colloid size (d_p), and mineral surface on colloid transport
- Differentiate those effects due to dispersion from those due to filtration and remobilization
- Accurately relate physical parameters (Q, d_p, $surface$) to interaction energies
- Define filtration probability and remobilization rate in terms of interaction energy

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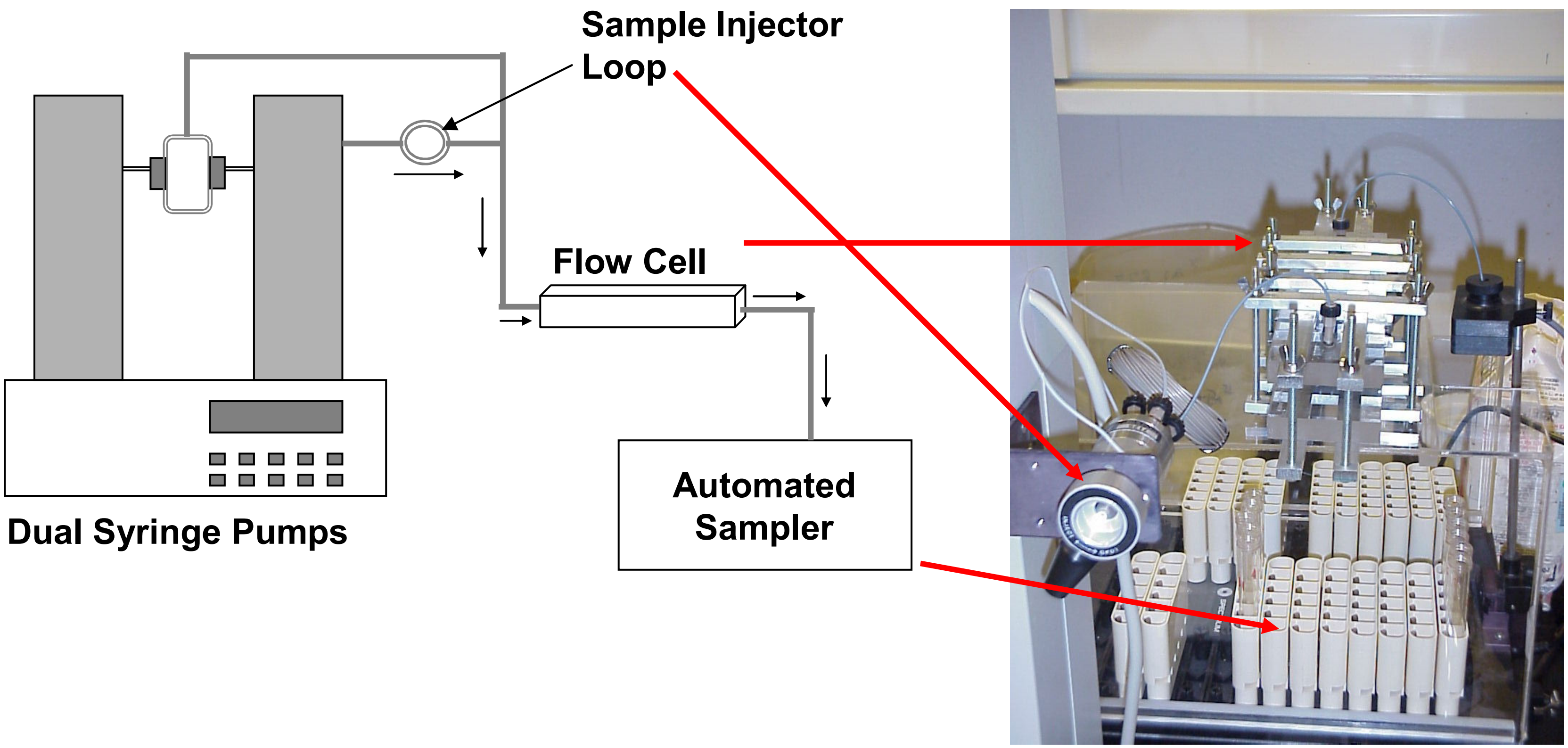
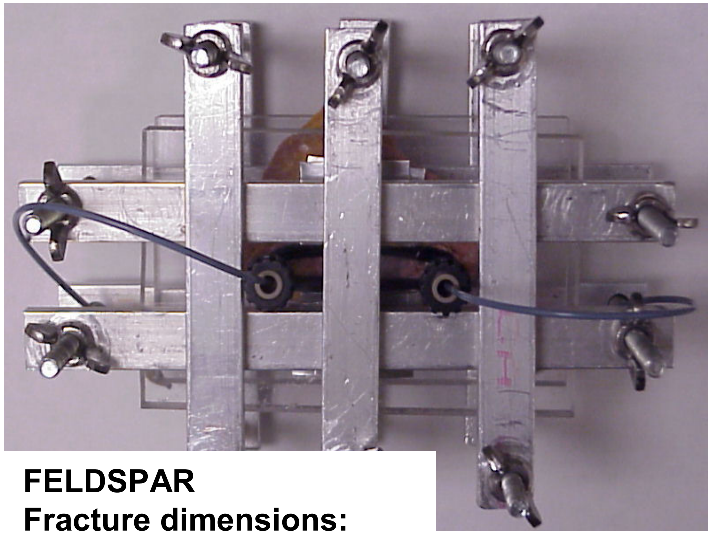
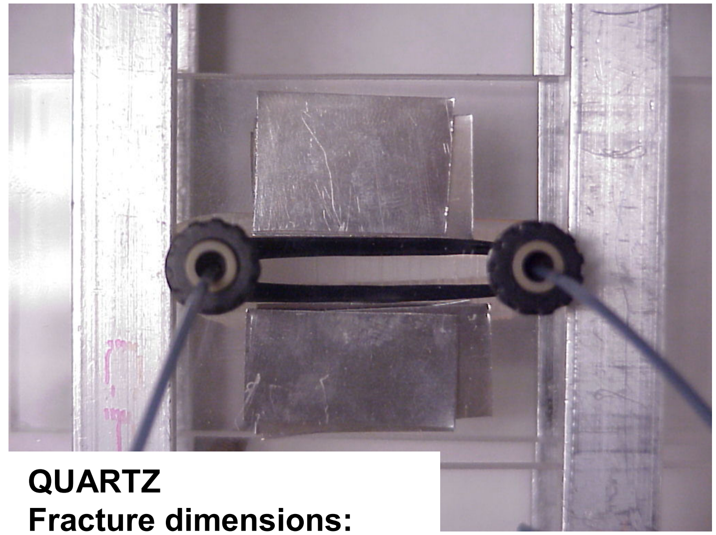
Experiment Apparatus



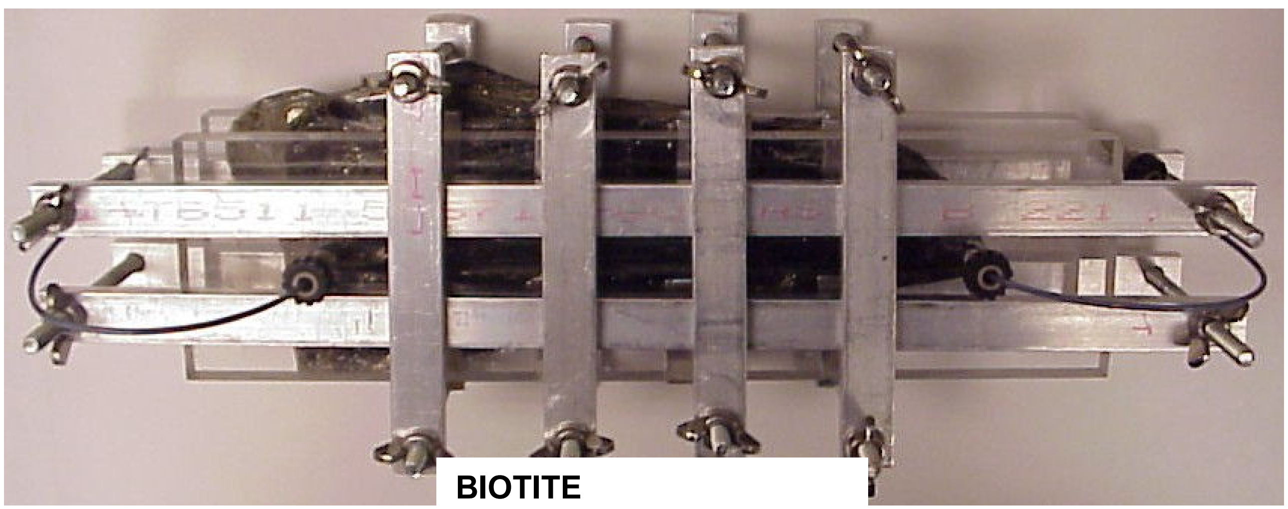
Flow Cells



FELDSPAR
Fracture dimensions:
3.2 cm × 4.25 mm × 1 mm

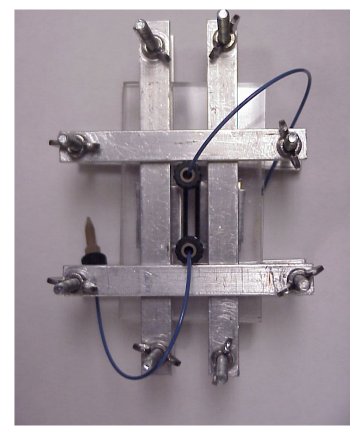


QUARTZ
Fracture dimensions:
4.0 cm × 4 mm × 1.1 mm



BIOTITE
Fracture dimensions:
16.0 cm × 4 mm × 1.1 mm

PLEXIGLAS control duplicate cells



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Interpreting Experiment Results

- **Primary goal** is to determine filtration probability and remobilization rate as a function of flow rate (Q), colloid size (d_p), and mineral surface type
- **Observe** different behavior between control (Plexiglas) and mineral
  - Transport in both systems is influenced by dispersion
- A **particle-tracking algorithm** run in inverse mode has been used to capture differences and estimate filtration probability/remobilization rate
- **Major challenge** arises in determining how to separate those effects due to dispersion (both systems) from those due to filtration and remobilization

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Numerical Methods - Physical Relationship

- In a non-reactive system, transport is controlled by advection, diffusion, and dispersion
- Recall:

$$D = \frac{kT}{3\pi\mu d_p}$$

Molecular Diffusion

$$D_{Taylor} = D + \frac{1}{210}\frac{\overline{u}^2 b^2}{D}\left(1 - \frac{d_p}{b}\right)^6$$

Taylor Dispersion

- D_{Taylor} is only valid for fully developed flow conditions, i.e. when the fracture length (L) exceeds an entrance length (L_e) given by:

$$L_e > \frac{6\overline{u}b^2}{\pi^2 D}$$

- For $L < L_e$, dispersion is defined by an effective dispersion coefficient, D_{eff}, that is bounded by D and D_{Taylor}

Numerical Methods – Numerical Relationship

- Characteristic Peclet number can be defined for each experiment:

$$Pe = \frac{\bar{u}L}{D} = \frac{3\pi\mu}{kT}\left(\frac{QL^2 d_p}{V_f}\right) \quad [-]$$

Q: injectant flow rate [L^3t^{-1}]
L: fracture length [L]
V_f: fracture volume [L^3]

- A relationship can be established between D_{eff} and Pe and can be used to distinguish colloid tailing due to dispersion from colloid tailing due to filtration and remobilization

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Experimental Methods

- Plexiglas flow cell system with conditions unfavorable for filtration
- Colloid size (d_p), flow rate (Q), and length (L) varied to achieve a reasonably large range of Peclet numbers (Pe)

Experiment	d_p (μm)	Q (ml/min)	V_f (ml)	L (cm)	b (mm)	C_0 (colloids/ml)	Pe (–)
P1	0.11	0.1	0.216	4.1	0.813	5.44×10^{10}	3.3×10^{6}
P2	0.11	0.1	0.486	16.0	0.813	5.69×10^{10}	2.2×10^{7}
P3	0.11	1.0	0.130	3.2	0.813	5.17×10^{10}	3.3×10^{7}
P4	0.11	0.5	0.361	8.1	0.813	5.56×10^{10}	3.8×10^{7}
P5	0.11	0.5	0.311	8.1	0.762	4.50×10^{10}	4.4×10^{7}
P6	0.043	1.0	0.479	16.0	0.813	9.06×10^{11}	6.5×10^{7}
P7	1.0	0.11	0.311	8.1	0.762	7.53×10^{7}	8.9×10^{7}
P8	0.043	1.0	0.471	16.0	0.914	7.84×10^{11}	9.0×10^{7}
P9	0.11	1.0	0.479	16.0	0.813	5.14×10^{10}	1.7×10^{8}
P10	0.11	1.0	0.471	16.0	0.914	5.19×10^{10}	2.3×10^{8}
P11	1.0	0.5	0.311	8.1	0.762	7.70×10^{7}	4.0×10^{8}
P12	1.0	1.0	0.574	16.0	0.813	7.70×10^{7}	1.5×10^{9}
P13	1.0	1.0	0.471	16.0	0.914	6.68×10^{7}	2.1×10^{9}

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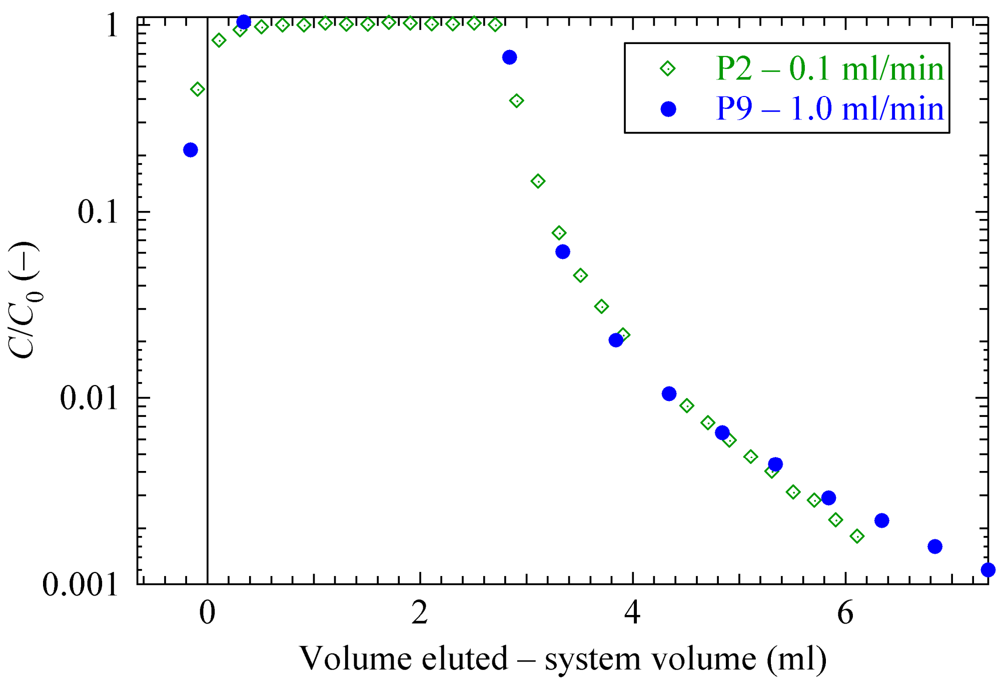
Experiment Results

Flow Rate (Q) Variations

- d_p = 0.11 µm
- L = 16 cm



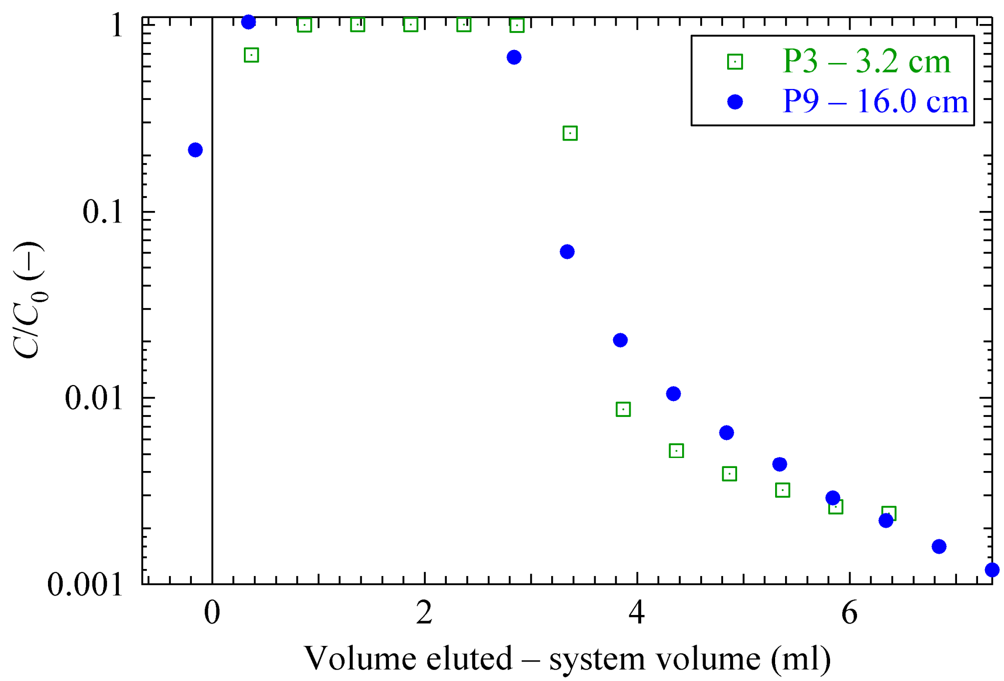
$D_{eff} = 1.3\times10^{-4}$ m²/s

$D_{eff} = 2.7\times10^{-4}$ m²/s

Experiment Results

Length (L) Variations

- Q = 1.0 ml/min
- d_p = 0.11 µm



$D_{eff} = 5.9\times10^{-5}$ m^2/s
$D_{eff} = 2.7\times10^{-4}$ m^2/s

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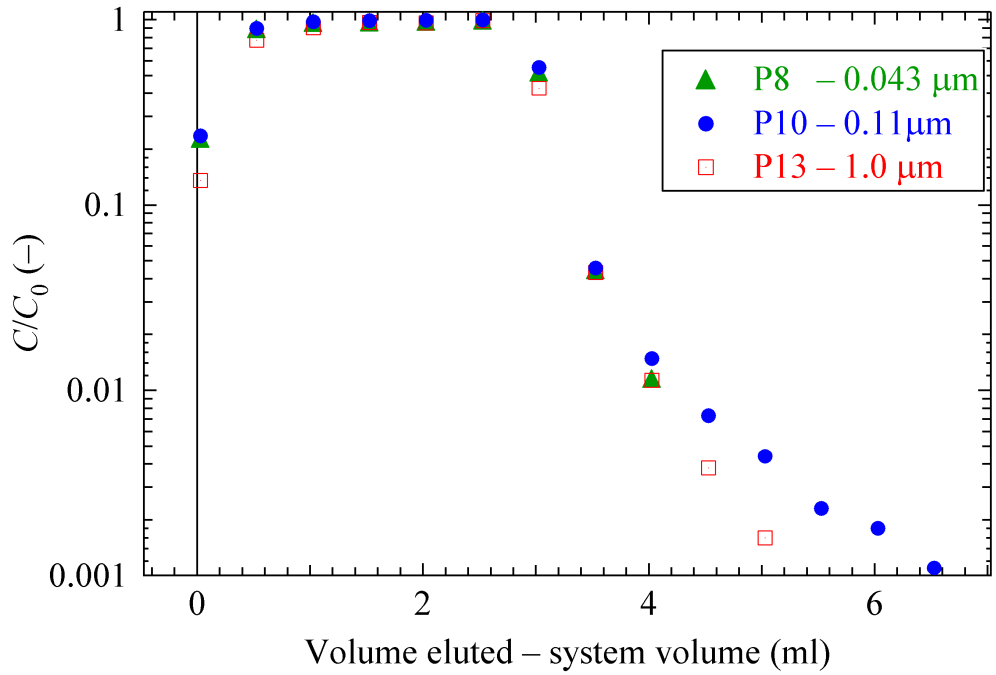
Experiment Results

Colloid Size (d_p) Variations

- Q = 1.0 ml/min
- L = 16 cm



$D_{eff} = 9.7\times10^{-5}$ m^2/s
$D_{eff} = 3.6\times10^{-4}$ m^2/s
$D_{eff} = 2.4\times10^{-4}$ m^2/s

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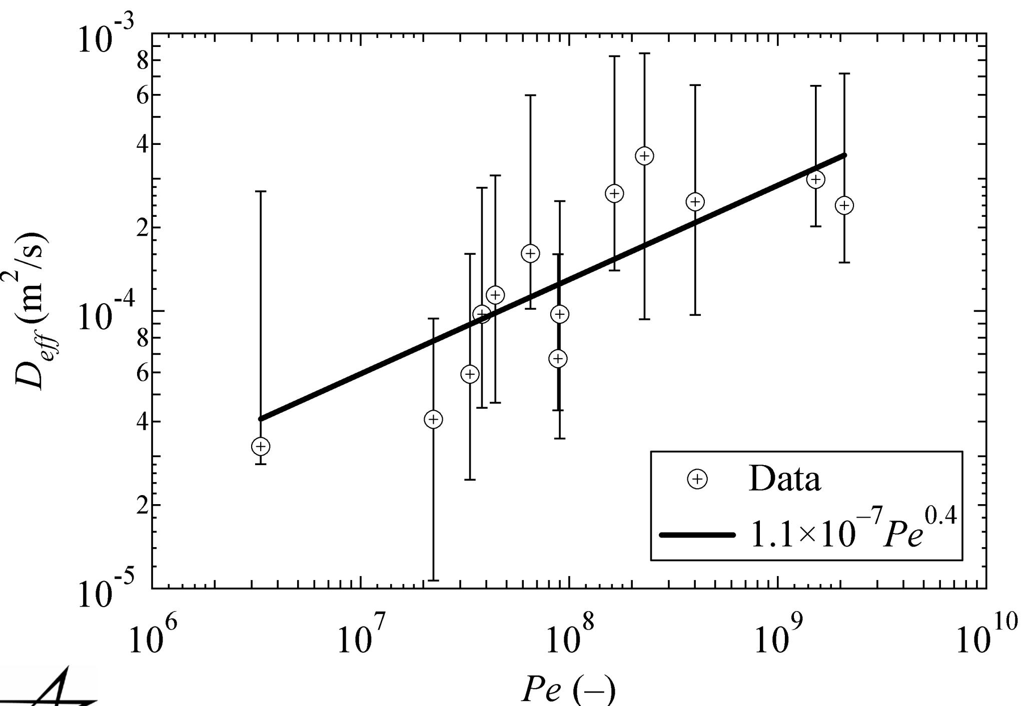
Numerical Results

D_{eff} versus Pe

- $D_{eff} = 1.1\times10^{-7} Pe^{0.4}$
- $R^2 = 0.72$
- Relationship can be used to differentiate non-reactive transport (i.e., dispersion) from reactive transport (i.e., filtration)



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Summary and Future Work

- Qualitatively and quantitatively observe increased tailing with increased flow rate and flow cell length
- No consistent trend associated with colloid size variations over the range investigated
- Series of experiments over Plexiglas (non-reactive) surface provided data to numerically establish a relationship between D_{eff} and Pe
- Experimental results over biotite, feldspar, and quartz surfaces can now be reevaluated using D_{eff} vs. Pe relationship
  - Tailing due to dispersion separable from tailing due to filtration and remobilization
  - Filtration and remobilization are only unknown parameters and can be estimated using well-developed particle-tracking code and PEST

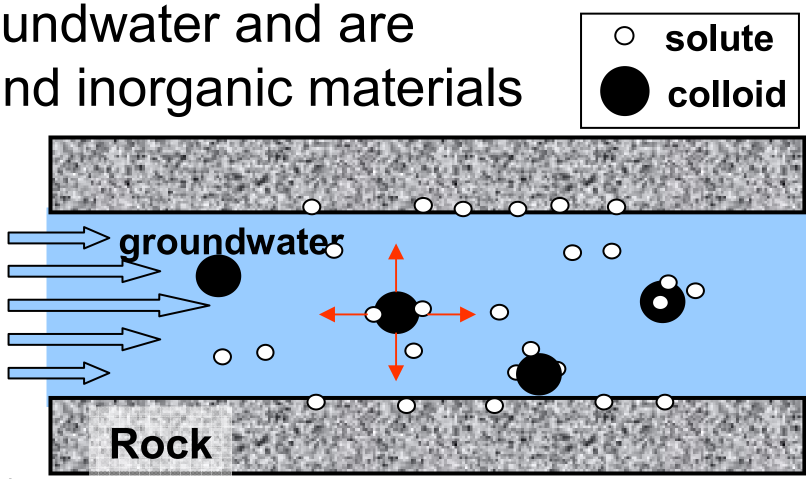
Questions?

McCarthy and Zachara, 1989

Extra Slides

Colloids: What and Why?

- What are colloids?
  - Particles with linear dimensions between 1 – 1000 nm
  - Particles with a high sorptive capacity
  - Particles that occur naturally in groundwater and are composed of a variety of organic and inorganic materials
    - Viruses, Bacteria
    - Clay and Mineral Fragments



- Why do we care about colloids?
  - Enhance contaminant migration
    - Colloids can travel faster than a conservative tracer in groundwater due to charge exclusion, size exclusion, and reduced matrix diffusion
  - Inhibit contaminant migration through filtration
    - Attachment
    - Settling

Why Are Colloids of National and International Interest?

- Colloid transport through fractures
  - Many radioactive waste repositories proposed in fractured media
  - Mechanisms are not clearly understood
- Enhanced radionuclide migration
  - Migration of plutonium and americium at Los Alamos National Laboratory
  - Radionuclide transport at the Nevada Test Site
- Japan Nuclear Cycle Development Institute (JNC)
  - Part of their high-level nuclear waste program
  - Interest in how colloids influence radionuclide transport
- Yucca Mountain Project (YMP)
  - A source of uncertainty for PA calculations
  - NRC has requested further study (Key Technical Issue)

Controls of Colloid Transport

- Physical
  - Advection
  - Diffusion ☆
  - Dispersion
    - Taylor dispersion
  - Hydrodynamic chromatography
  - Adsorption (of solute onto colloid)
  - Surface attachment (of colloid)
  - Sieving
  - Gravity Settling ☆
- Chemical
  - Surface chemistry of colloids
  - Surface chemistry of media
  - Electrostatic forces
  - Van der Waals forces
  - Ionic strength of solution

☆ **Indicates physical processes that can transport colloids to the fracture wall**

Red indicates processes *explicitly* considered in the numerical modeling

Blue indicates processes *implicitly* considered in the numerical modeling

Relevant Physical Controls

- Advection
  - Transport due to flow velocity
- Diffusion
  - Random Brownian motion described by the Stokes-Einstein equation:

$$D = \frac{kT}{3\pi\mu d_p} \quad [L^2 t^{-1}]$$

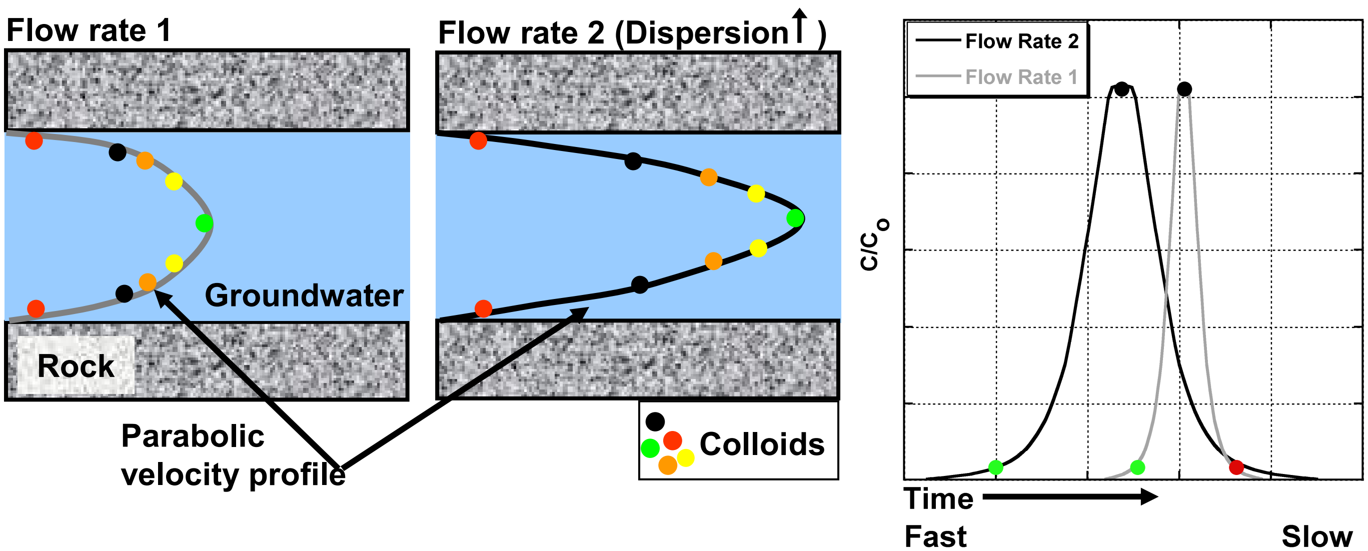
k: Boltzmann's constant $[ML^2T^{-1}t^{-2}]$
T: absolute temperature [T]
μ: kinematic viscosity of the interstitial fluid $[ML^{-1}t^{-1}]$
d_p: particle size [L]

- Taylor Dispersion
  - Spreading parallel to center streamline

$$D_{Taylor} = D + \frac{1}{210}\frac{\overline{u}^2 b^2}{D}\left(1 - \frac{d_p}{b}\right)^6$$

$\overline{u}$: average interstitial fluid velocity $[Lt^{-1}]$
b: fracture aperture [L]

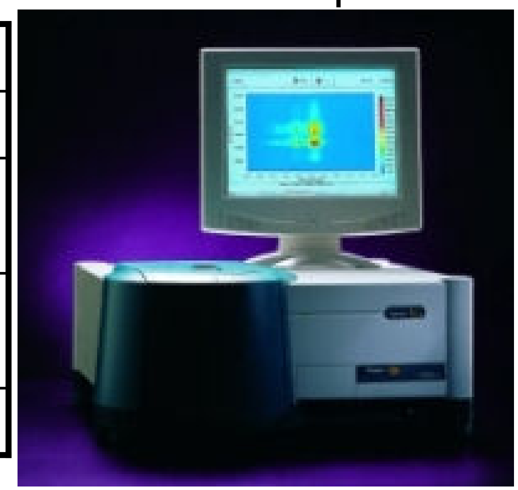
Taylor Dispersion



Tracers and Detection

- **Cary Eclipse Fluorescence Spectrophotometer**
  - TransFluoSpheres® Carboxylate-Modified Fluorescent Microspheres

Size (μm)	0.043	0.11	1.0
Excitation/Emission (nm)	488/685	488/690	488/650
Initial Concentration (particles/ml)	$\sim 9\times10^{11}$	$\sim 5\times10^{10}$	$\sim 8\times10^{7}$
Detection Limit (particles/ml)	$\sim 2\times10^{9}$	$\sim 9\times10^{6}$	$\sim 3\times10^{3}$
Error	5–10%	5–10%	~5%



- **Dionex Ion Chromatograph (DX 600)**
  - Cl^- as NaCl

Initial Concentration (mg/l)	1,000
Detection Limit (mg/l)	~1 mg/l
Error	<10%

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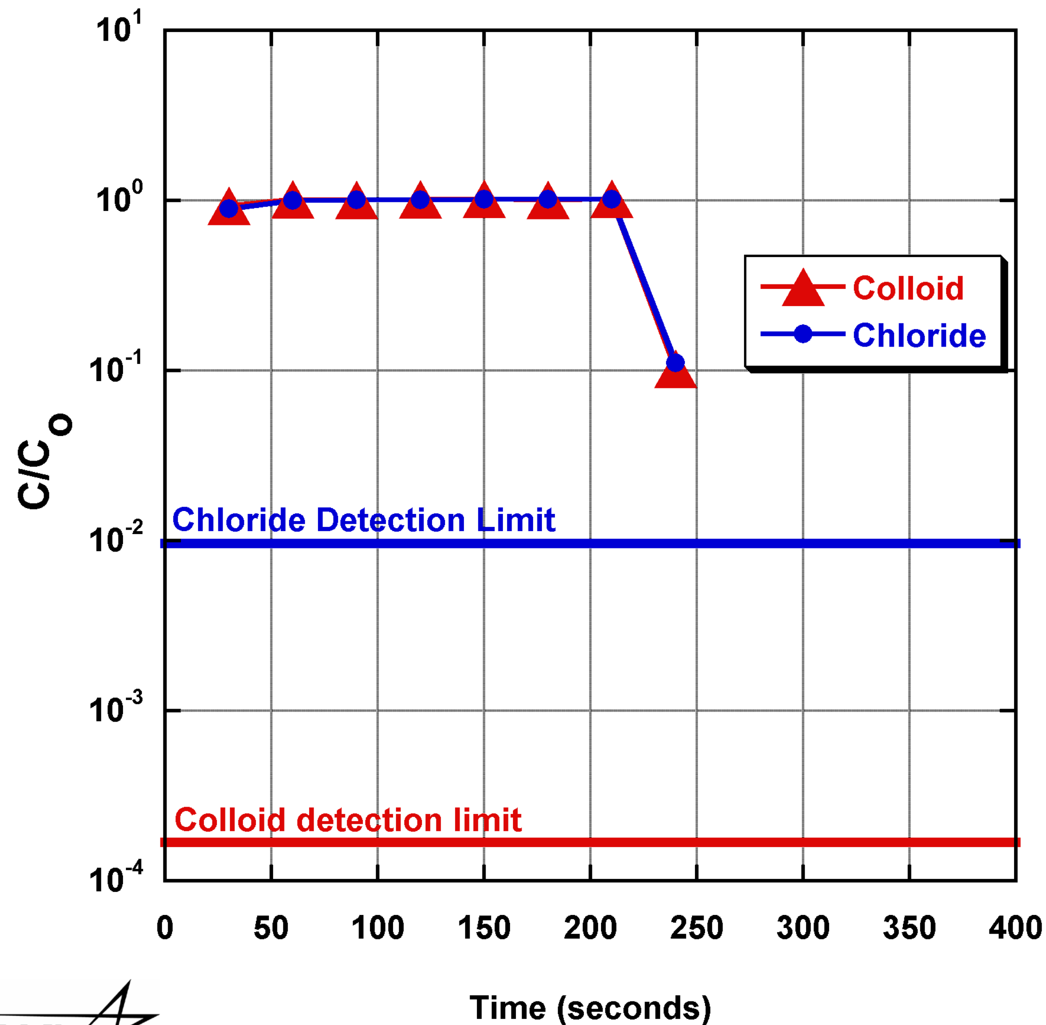
Experiment Results

Colloid and Chloride Behave Similarly in Tubing



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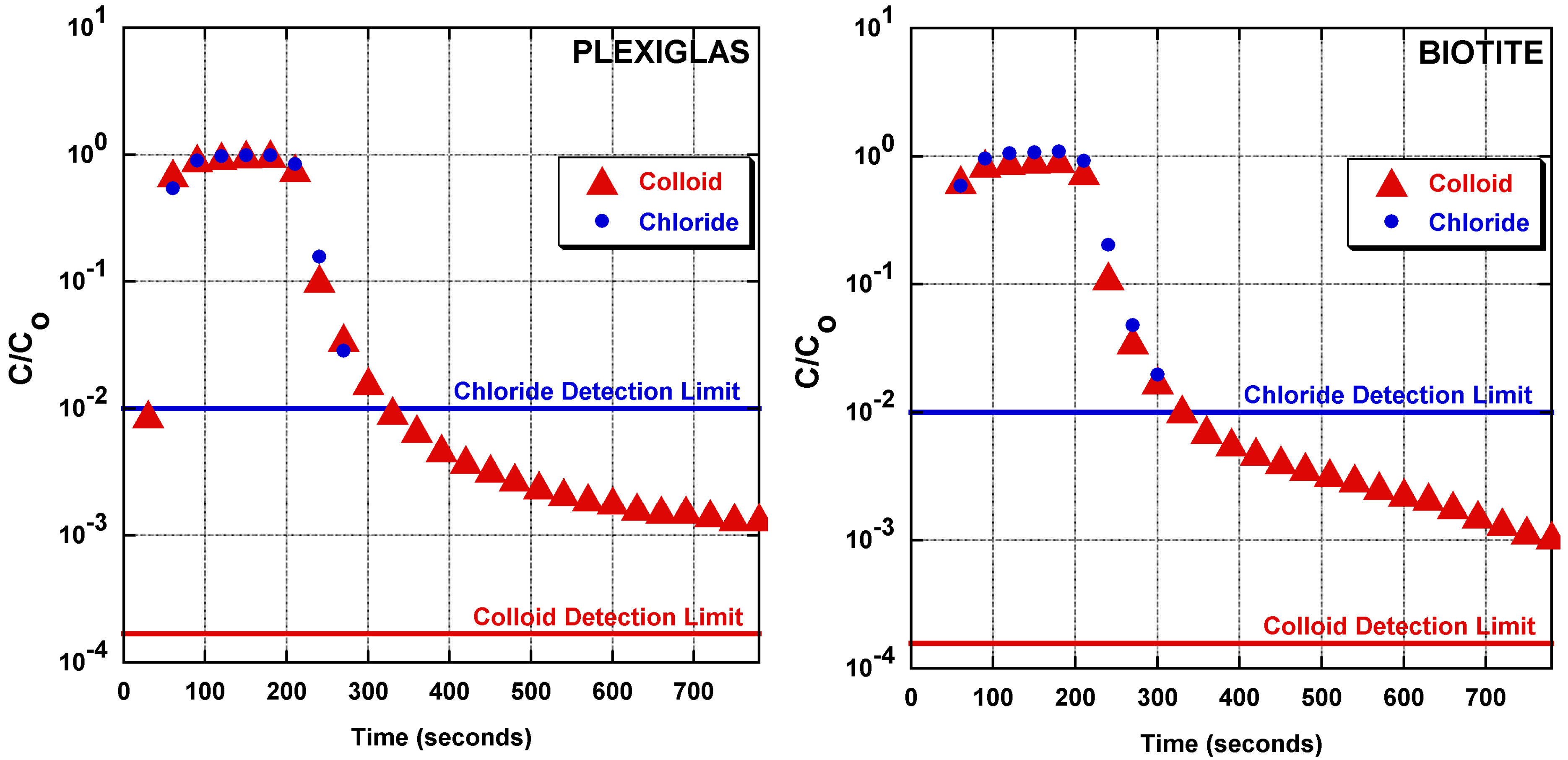
Experiment Results

Colloids Subject to More Tailing than Chloride



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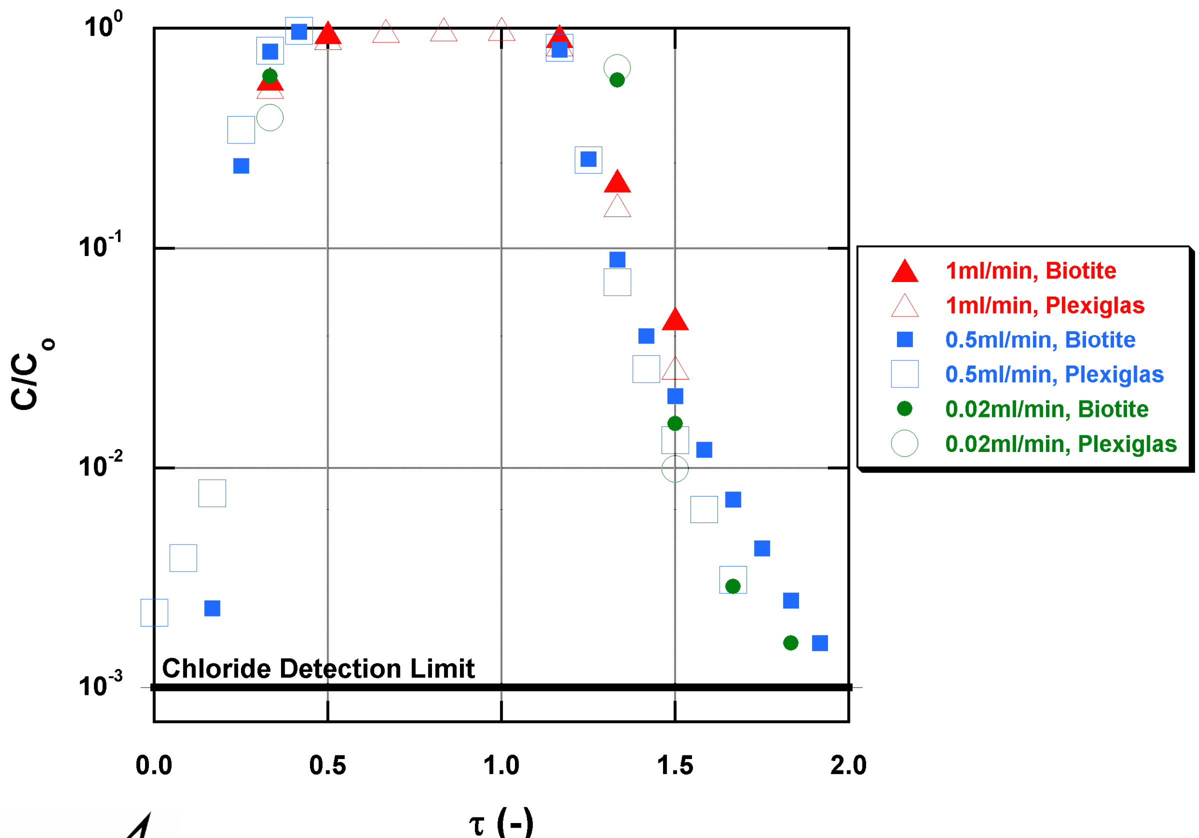
Experiment Results

Reproducible Chloride Results

- Initial chloride concentration = 100 mg/l
- Slight increase in tailing with increasing flow rate



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Numerical Methods

- Colloids and Chloride tracked in one dimension
  - Simplification justified by James and Chrysikopoulos (2003)
  - Requires the use of effective parameters as follows:

$$x^{m+1} = x^m + U_{eff}\Delta t + Z(0,1)\sqrt{2D_{eff}\Delta t}$$

x^{m+1}: coordinate in the flow direction at time $m+1$ [–]

Δt: time step [–]

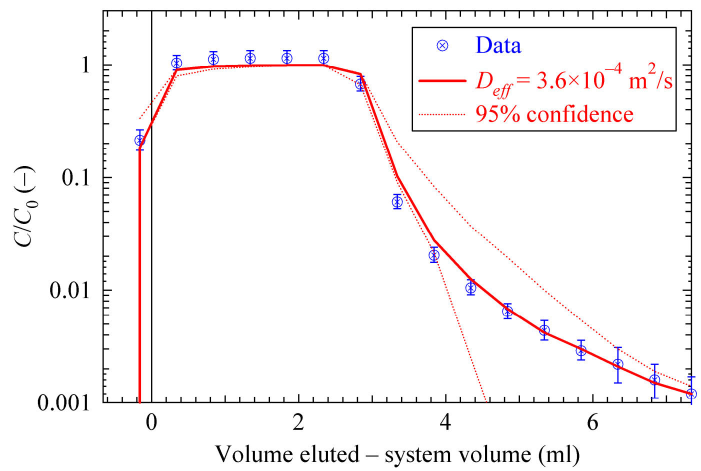
$Z(0,1)$: random selection from the standard normal distribution [–]

U_{eff}: effective interstitial fluid velocity [Lt^{-1}]

$$U_{eff} = \overline{u}\left[1 + \frac{d}{b} - \frac{1}{2}\left(\frac{d}{b}\right)^2\right]$$

Numerical Simulations

- Particle-tracking algorithm
  - Maps the location of particles as a function of time, based on a defined set of parameters
  - Transport processes include advection, diffusion, and effective dispersion
- Inverse simulations
  - Parameter ESTimation (PEST) by Watermark Numerical Computing
  - Used to estimate D_{eff} for each experiment



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Experiment Results

No Permanent Filtration of Colloids

Experiment	Mean % recovery	Max % recovery	Min % recovery
P1	48%	50%	47%
P2	100%	106%	95%
P3	100%	103%	97%
P4	98%	102%	94%
P5	85%	90%	81%
P6	89%	92%	87%
P7	63%	93%	76%
P8	93%	96%	90%
P9	110%	113%	105%
P10	95%	102%	88%
P11	83%	121%	99%
P12	98%	109%	87%
P13	87%	100%	76%